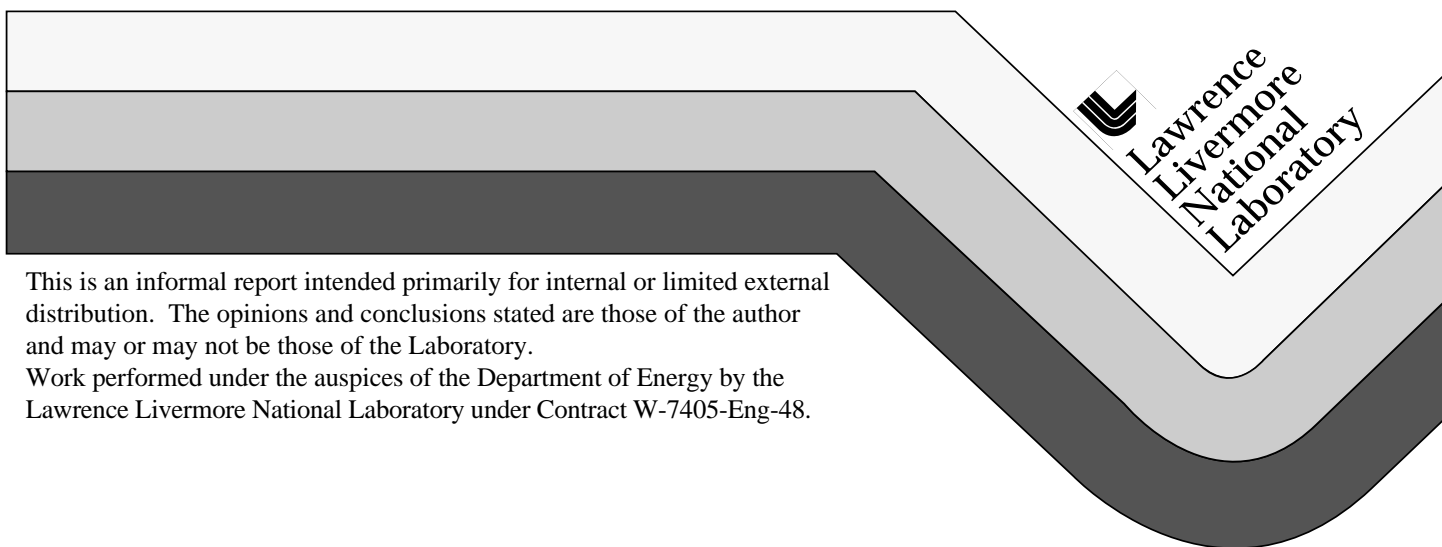


Synthesis and Scale-up of New Explosives

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Abstract

We are investigating the synthesis of new energetic materials comprised of nitro- and amino-substituted heterocycles. Our efforts may be divided into two main areas of interest selected in response to the needs of the Departments of Defense and Energy: (1) insensitive energetic materials which approach HMX in energy and (2) new energetic materials which calculate to have more energy or power than CL-20. We have synthesized the new, insensitive, energetic heterocycles 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105) and 4-amino-3,5-dinitropyrazole (LLM-111) with 80-85% the energy of HMX and excellent thermal stability. LLM105 also has excellent chemical stability. We have synthesized enough material for evaluation by the detonator community. We have begun an investigation of a series of nitro-substituted, bicyclic heterocycles which calculate to have more energy than CL-20. This is a collaborative effort with our theoretical modeling group in which the structures of the target molecules were generated by Laurence Fried and the synthetic schemes were developed by LLNL's synthesis group. The synthesis of insensitive energetic materials by the Vicarious Nucleophilic Substitution (VNS) of hydrogen, which incorporates 1,1,1-trimethylhydrazinium iodide (TMHI) as an aminating reagent for nitro-substituted aromatic and heterocyclic compounds, is a continuing effort in our program.

Introduction

The Synthesis Group of the Energetic Materials Section at LLNL is dedicated to the development of new, high energy materials. Our efforts are divided into several areas of interest: (1) new, insensitive compounds which perform better than 2,4,6-trinitrotoluene (TNT); (2) new energetic compounds which possess more energy than 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) or CL-20; (3) synthesis of new oxidizers for propellant application; and (4) new energetic polymer ingredients.

Our group has the capability to synthesize and develop new compounds from the milligram to the multi-kilogram scale. In addition, we are closely coupled with our theoretical modeling and experimental testing groups, providing the capability to quickly obtain performance measurements and equation of state information on new compounds with as little as 50 g of material.

Our research is directed to respond to the needs of the DoD and DOE community. Many of our projects are done in collaboration or discussion with groups in the DoD community, including NavAir-China Lake and NavSea-Indian Head. Our current project in the synthesis of amino- and nitro-substituted heterocycles, which uses the VNS of hydrogen as a method to introduce amino groups onto nitro-substituted heterocycles, has been performed in collaboration with Bill Wilson at NavAir-China Lake who is using the same approach to make insensitive energetic materials. The VNS project originated out of a demilitarization project which was looking at methods to convert surplus explosives into higher value products which, in turn, used ideas first developed under our Office of Munitions Program.

The areas of interest which we have identified are all directed to improving the safety and performance of current and future weapon systems. As an example, the development of new energetic materials possessing more energy than HMX has been of critical importance to weapon designers for some time. Although HMX has very good performance and safety characteristics, it has been found lacking in some applications where energy per unit volume is critical. The development of a more energetic HE would provide alternatives in these applications. The development of new oxidizers for propellant application will lead to an increase in I_{sp} and range of new weapon systems, while new polymer ingredients for thermoplastic elastomers will aid in the demilitarization of weapons. With the growing concern for safety, the development of a more insensitive and energetic replacement for TNT and RDX has also been a critical area of research in recent years.

The nature of our synthetic research program demands that the synthesis and characterization of the performance of a new energetic material be considered a payoff. We will provide performance and sensitivity information about the new energetic material to the DoD and DOE for their evaluation of its usefulness. Additionally, information gained on new materials will help improve predictive capabilities and point out anomalies due to structural features, thus guiding the design of future generation target materials. We have developed a true collaborative effort with our theoretical modeling group. The structures of the target molecules in our high energy molecule effort were generated by Laurence Fried of our theoretical modeling group, and the syntheses were developed by the synthesis group.

Results

Our synthetic work in the past year was divided into two main thrust areas: (1) synthesis of new energetic compounds which outperform HMX without increase in sensitivity, and (2) synthesis of new insensitive energetic explosives (IHEs) with more energy than TNT. From this latter effort we have synthesized 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105),¹ an insensitive energetic material with 30% more energy than TNT. The energy content and thermal stability of this material make it very interesting for several applications, including insensitive boosters and detonators. We have been investigating a new approach to the synthesis of LLM-105 which is more environmentally friendly and has a shorter reaction sequence than the previous method. This involved the condensation of alloxan monohydrate and 5,6-diaminouracil in water to yield 2,4,5,7-tetrahydroxy[5,4-g]pyrimidopteridine,² which

was treated with aqueous sodium hydroxide at 170°C in a Parr pressure vessel to yield 2,6-diamino-3,5-dicarboxypyrazine.³ We have attempted to nitratively decarboxylate this material to 2,6-diamino-3,5-dinitropyrazine (ANPZ) but have thus far been unsuccessful (Fig. 1). This investigation of this synthesis will continue, along with alternative methods to synthesize LLM-105.

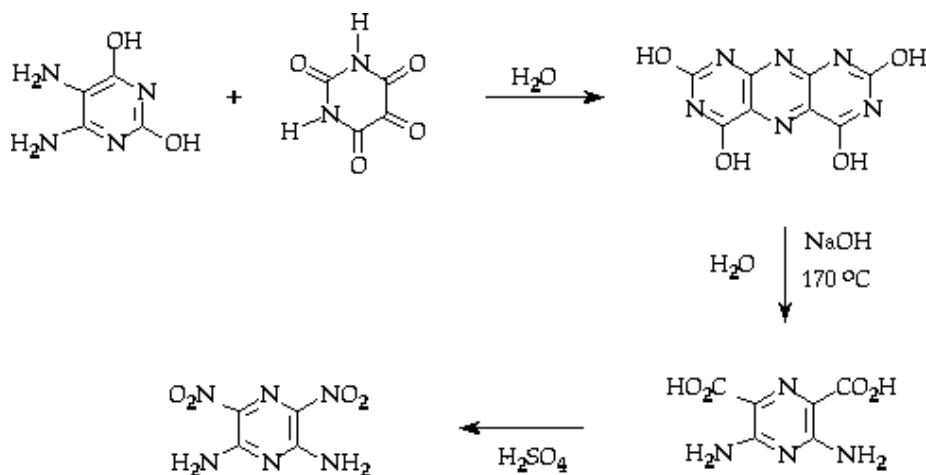


Figure 1. Alternative approach to the synthesis of ANPZ and LLM-105.

We have had some excellent results using our VNS⁴ approach to the synthesis of new insensitive energetic materials. The VNS approach incorporates the use of an aminating agent in the presence of base to introduce amino groups onto electrophilic aromatic rings. This is analogous to a Friedl-Crafts reaction in that the amino group formally replaces a hydrogen on the aromatic ring. In FY94, we successfully converted TNT to 2,5-diamino-2,4,6-trinitrotoluene (DATNT), an insensitive explosive of interest to the DoD, in one step at ambient temperature using 4-amino-1,2,4-triazole (ATA).⁵ This is a significant improvement over the previously published procedures for the synthesis of this compound, which required four or five steps and an expensive starting material such as 3,5-dichloroanisole.⁶ We also investigated the VNS approach for the synthesis of 1,3,5-triamino-2,4,6-trinitrobenzene and 1,3-diamino-2,4,6-trinitrobenzene from picramide.⁷

In FY95, we developed a new VNS aminating reagent, 1,1,1-trimethylhydrazinium iodide (TMHI), which may be synthesized by alkylation of the surplus propellant found in million-pound quantities in the former Soviet Union, *uns*-dimethylhydrazine (UDMH) (Fig. 2). It may also be synthesized directly from the inexpensive reagent, hydrazine, by alkylation with methyl iodide in the presence of base. This reagent acts analogously to ATA, although studies have shown it to be significantly more reactive. In a comparison test, TMHI converts picramide to TATB by stirring overnight at room temperature (although actual time to completion is probably around 3 h) while ATA takes at least 30 h for complete conversion. In FY96, we demonstrated the use of TMHI in the synthesis of DATNT from TNT in one step in 50% yield.

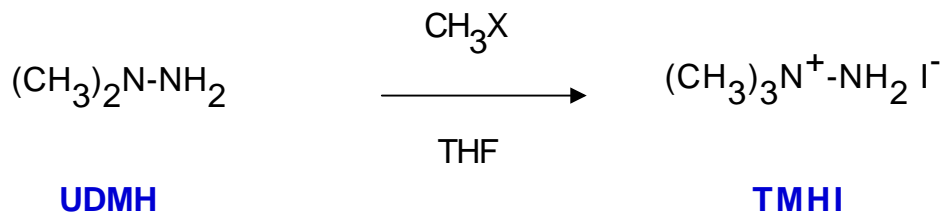


Figure 2. Synthesis of the new VNS aminating reagent, 1,1,1trimethylhydrazinium iodide (TMHI).

Our group was the first to demonstrate the use of TMHI in a VNS reaction and has provided the basis for an innovative approach to the synthesis of insensitive energetic materials. Previous methods for the synthesis of insensitive energetic materials generally relied on nitration of amino-substituted aromatic species or the reaction of chlorinated nitroaromatics with ammonia. Our VNS method allows amination of polynitro-substituted aromatics by the formal displacement of hydrogen, thus eliminating the need for chlorinated aromatic species. This is especially important with the call for elimination of chlorinated species from the industrial sector because of their adverse environmental effects. The VNS method also allows the synthesis of insensitive energetic materials not accessible by the previously described methods.

Using the VNS method with TMHI, we have synthesized the previously unknown 4-amino-3,5-dinitropyrazole (LLM-111), a potentially insensitive energetic material with 80% the energy of HMX. This is significant because LLM-111 could not be synthesized by ordinary methods. During our study of the scope and limitations of TMHI as a VNS aminating reagent we found that the number of amino groups which may be added to the electrophilic aromatic ring is equal to the number of nitro groups present on the substrate. This observation led us to investigate the amination of 3,5-dinitropyrazole (DNP), which carries an acidic hydrogen, to give LLM-111. We reasoned that the acidic proton on DNP would initially react with one equivalent of base to form a stable nitronate anion leaving the second nitro-group available to participate in the VNS amination. We found the reaction of DNP with TMHI in the presence of excess potassium *tert*-butoxide gave LLM-111 in 70% yield (Fig. 3). This allowed the synthesis of LLM-111 without the need for a protecting group for the pyrazole proton and demonstrated a rare example of a nucleophilic substitution reaction on an aromatic ring already bearing a negative charge. The LLM-111 was isolated as a 1:1 complex with dimethylsulfoxide with a crystal density of 1.608 g/cc,⁸ and its structure confirmed by x-ray crystallographic analysis. We have found that refluxing in water breaks up the complex and crystallizes white cubes. An x-ray crystallographic analysis showed this material to be a 1:1 complex of LLM-111/ H₂O with a crystal density of 1.72 g/cc.⁸ We are in the process of evaluating the safety and performance characteristics of this new compound.

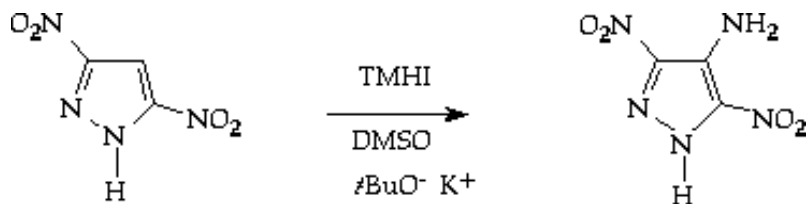


Figure 3. Synthesis of 4-amino-3,5-dinitro-1H-pyrazole (LLM-111).

The efficacy of TMHI as a VNS aminating reagent was tested by the reaction with a series of 3-substituted nitrobenzenes and published in the *Journal of Organic Chemistry*.⁹ This study provided the first indication of the superior reactivity of TMHI compared to ATA, with the product distribution consisting of all regioisomers in ratios which track the relative electron density distribution for each substrate.

We have continued our investigation of the synthesis of several nitro- and amino-substituted azoles. These target compounds calculate to have 80-95% the energy of HMX and are predicted to be relatively insensitive materials. The syntheses are based on VNS chemistry in which known polynitroazoles will be aminated with TMHI. We have been concentrating on the synthesis of a series of amino-substituted polynitropyrroles (Fig. 4). Our approach involved using both protected and nonprotected polynitropyrroles as substrates for amination with TMHI. We have attempted the amination of both 1-*t*-butyl-2,4-dinitropyrrole and 1-*t*-butyl-2,3,4-trinitropyrrole yielding only recovered starting material. We have synthesized both the 2,5- and 2,4-dinitropyrrole and are currently investigating the amination of these materials.

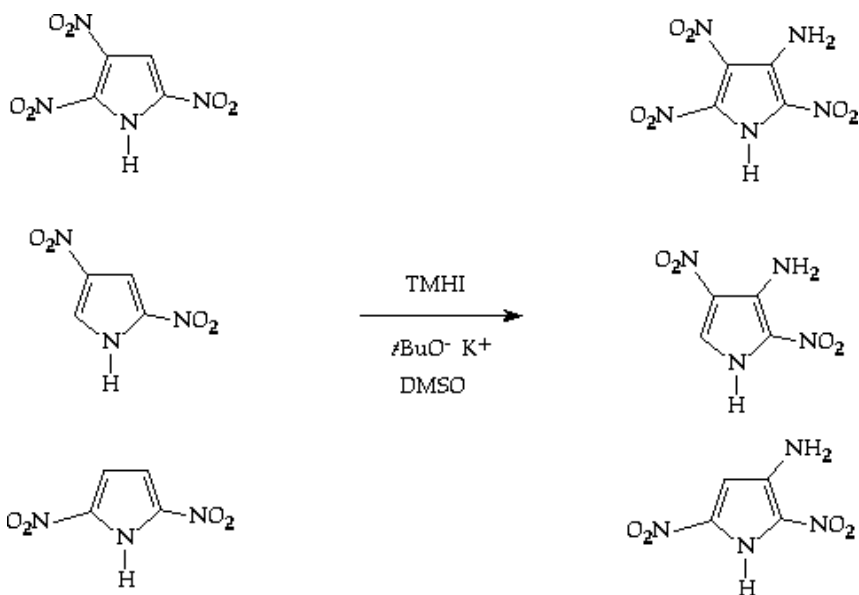


Figure 4. Amination of polynitropyrroles with TMHI.

We have begun an investigation of the synthesis of several energetic heterocycles which calculate to have more energy than CL-20. (Fig. 5). These target molecules are all planar, high nitrogen, zero-hydrogen nitroazoles. They are oxygen balanced to CO_2 and should have a

significant energy contribution from their high heat of formation. We have outlined synthetic routes to each of these based on literature precedence. We concentrated our initial efforts on the synthesis of 4,5-diamino-2-phenyl[1,2,3]triazole,¹⁰ an important intermediate for two of our target molecules. We investigated new methods for the synthesis of this material because reported methods use the highly toxic gas, cyanogen, as the starting material. We have chosen to use thiooxamide,¹¹ a readily available, inexpensive starting material, as a cyanogen surrogate and follow procedures similar to those used with cyanogen (Fig. 6). We have also been investigating the synthesis of 3-bromo-4-formyl-1-tosylpyrazole as an intermediate to the bipyrazole target compound. Work on these two syntheses continue.

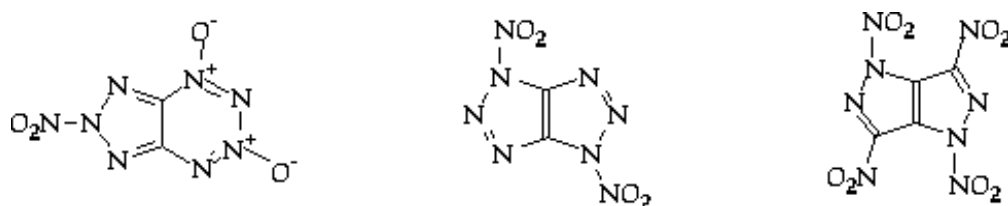


Figure 5. Target molecules with calculated energy greater than CL-20.

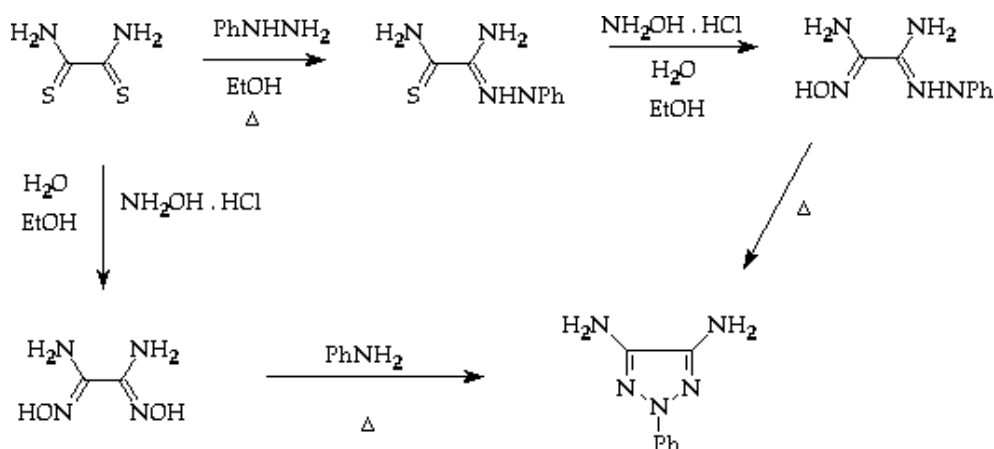


Figure 6. Synthesis of 4,5-diamino-2-phenyl[1,2,3]triazole from thiooxamide.

Conclusions

We have developed a synthesis program which is designed to respond to the needs of the DoD, concentrating on the synthesis of new energetic materials which may replace TNT and CL-20 or HMX in future weapon systems. We have synthesized two new, insensitive energetic materials, LLM-111 and LLM-105, with 80-85% the energy of HMX.

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